Atmospheric Pollution Research 5 (2014) 677-685

Atmospheric Pollution Research
www.atmospolres.com

The traffic linked urban ambient air superfine and ultrafine PM_1 mass concentration, contents of pro–oxidant chemicals, and their seasonal drifts in Lucknow, India

Mukesh Kumar Verma [1,2], Lalit Kumar Singh Chauhan [1], Sarwat Sultana [2], Sushil Kumar [1]

[1] *Environmental Carcinogenesis Laboratory, CSIR–Indian Institute of Toxicology Research, MG Marg, P Box 80, Lucknow–226001, India*
[2] *Medical Elementology and Toxicology Division, Jamia Hamdard University, New Delhi, India*

ABSTRACT

The anthropogenic $PM_{2.5}$ in ambient air is implicated in the increased health risks and morbidities of urban subjects. However in the literature, there is a limited information on mass concentrations and size segregated chemical profile of ultrafine and superfine PM_1 fractions of traffic linked urban ambient air. The size, and the adsorbed chemicals, and response to seasonal change in this submicron range of particles have seldom been studied so far. We have looked into these aspects in urban ambient air of Lucknow Uttar Pradesh India. A 10–stage MOUDI cascade impactor sampled the superfine ($PM_{0.56}$, $PM_{0.32}$, $PM_{0.18}$) and ultrafine particles ($PM_{0.1}$, $PM_{0.056}$) distributed in traffic linked ambient air. We studied their morphology, mass concentrations, the adsorbed metal contents and organic chemical moieties using TEM, gravimetric analyses, AAS, and FTIR spectroscopy. A change in their contents and profile with season was also examined. Results revealed spherical and fractal shapes of $PM_{0.1}$, 50 nm–2 µm size range of $PM_{0.56}$ fractions, and 10–100 nm size range of constituent spherules. Gravimetric analyses disclosed mass concentrations and multifold increases in their levels in winter. Cr, Cd, Ni, Pb and transition element Cu, Fe were found to be present in the studied particles. The presence of aliphatic and aromatic hydrocarbons with hydroxyl, carbonyl, and ketone groups were also found and displayed changes in their levels with season. Presence of organonitrate compounds indicated the role of submicron and nanosize particulates in secondary aerosol formation also. Results are important for epidemiological studies and public policy on superfine and ultrafine particulate matter in urban ambient air for identification of toxicity risk or health hazard, air quality monitoring and regulation.

Keywords: *Ultrafine, superfine, nano–particulate matter, carcinogen, transition metal, organonitrate*

Corresponding Author:
Sushil Kumar
☎ : *+91-0522-222-7586 Ext. 311*
☏ : *+91-0522-262-8227*
✉ : *sushilkumar@iitr.res.in*
sushilkumar.iitr@gmail.com

Article History:
Received: 16 December 2013
Revised: 17 April 2014
Accepted: 21 May 2014

doi: 10.5094/APR.2014.077

1. Introduction

The urban ambient atmospheric aerosol in outdoor air pollution is a complex mixture of superfine and ultrafine particulate matter (PM_1), the adsorbed chemicals, and the water vapor (Oberdorster and Utell, 2002; Mauderly and Chow, 2008). Accumulating evidences suggest it to be a perilous or even hazardous factor contributing to increases in cardiopulmonary disorders, skin diseases, lung cancer, and mortality in urban subjects and also to exacerbations of adverse health effects (Dockery et al., 1993; Stone et al., 2007; Strak et al., 2012; Kumar et al., 2013). The contributory role is feared by its greater number concentrations, large surface areas, low mass concentrations, and an array of adsorbed toxicants possibly of pro–oxidant potential present in urban ambient air.

Submicron particulate matter can deposit deep in lower respiratory tract (Kreyling et al., 2006) and escape the natural clearance mechanisms of tissues. This possibility may result in long–term retention of PM_1 and their adsorbed chemicals to present the threat of oxidative damage culminating into risk of toxicity. Respirable particulate matter of relatively larger sizes (PM_{10} and $PM_{2.5}$) and associated trace metals are known to be hazardous to human health. This is mostly due to their potential of generating Reactive Oxygen Species (ROS) and oxidative stress causing DNA damage and cytotoxicity (WHO, 2006; Roberts et al., 2010; Meister et al., 2012; Strak et al., 2012; Deshmukh et al., 2013; Valavanidis et al., 2013).

There is a limited amount of information in literature on mass concentrations, physico–chemical analyses and the hazard analyses of the superfine and ultrafine particulate matter of urban ambient air (Stone et al., 2007; Park et al., 2008; Lu et al., 2011; Deshmukh et al., 2013; Kumar et al., 2013). Presumably, it is due to the apprehension of insufficient mass collection in their sampling from urban ambient aerosol. Sporadic reports reveal only the number concentrations and profile of adsorbed toxic chemicals like metals, hydrocarbons, dioxins, and nitro–PAHs (Voutsa and Samara, 2002; Park et al., 2008). The source of PM_1 pollution in urban ambient air is largely low–mass aerosol from diesel combustion exhausts.

We have investigated the mass concentrations of superfine and ultrafine PM_1 fractions, the adsorbed chemicals and their particulate size based distribution pattern in urban aerosol. We examined also their sensitivity to change in seasons. Affiliation of changes in superfine and ultrafine PM_1 mass concentrations with changes in weather conditions is unknown. We studied the ambient air levels of ultrafine fractions in the urban aerosol of a roadside location in Lucknow, the capital city of Uttar Pradesh (north province) State of India. Its coordinates are 26.847°N 80.947°E as indicated by GEO URI (26°50′ 49.2″N, 80°56′ 49.2″E as indicated by World Geodetic System, WGS 84). The level of auto exhaust pollution could be gauged from the information that (a) city added 186 000 automobiles exclusively in 2009–2011 (GOI, 2013), (b) approximately 4.5 million subjects populated the city, and (c) every day nearly a million commuters sought transport

across the city area of ~300 km^2 (population density 2 011/km^2). Lucknow is largely a residential and commercial city. Industrial establishments are rare and located 10–15 km away from the monitoring point.

2. Materials and Methods

2.1. Sampling and monitoring locations

A high density traffic location (approximately 25 000 vehicles per day) in the urban area of Lucknow was monitored. The aerosol samples were collected in the month of October (autumn) and December (winter) in 2011 and March (spring), April (summer), and May (summer) in 2012. The traffic linked ambient air was sampled in an outdoor area. A roadside location on an arterial street on the river bank was the sampling spot as illustrated in Figure 1 (radial distance of 100 m from the landmark High Court). The sampling station was located at an elevation of 1.5 m above the ground level to simulate the inhalation exposure conditions for humans. Sampling was done in inhalable zone and in non–dusty areas. Outdoor activity included around–the–clock movement of both heavy and light commercial vehicles (more intense during daytime working hours), vehicular traffic (gasoline driven motor-cycles, CNG driven three–wheelers, gasoline/diesel driven four–wheelers) at the sampling location. The automobile exhaust emissions and the roadside kiosk were the major source of pollution, mixed with automobile–tyre scrubs. The air drift of river–bank–dust dispersion was not a contributor to the monitored urban aerosol for the larger size of suspended particulate matter.

Figure 1. *Map of Lucknow (a diagrammatic sketch).*

2.2. Sampling

MOUDI cascade impactor (Micro–orifice uniform deposit impactor, MOUDI–NR 110; MSP Co., Minneapolis, MN, USA), a 10 stage impactor, was used to sample fractions in a range of sizes. Superfine particles ($PM_{1.8}$, PM_{1}, $PM_{0.56}$, $PM_{0.32}$, and $PM_{0.18}$) and ultrafine particles ($PM_{0.1}$, and $PM_{0.056}$) were collected. The particles were collected for 24 h on pre–weighed 47 mm aluminum foil at a flow rate of 30 L/min. Particulate matter was collected for 8 h (8 AM to 4 PM) daily for 3 days on the same foil. Thus, the 8 h x 3 day collection schedule constituted one 24 h monitoring activity. It was repeated three times over 9 day period with a fresh 47 mm aluminum (Al) foil to complete 3 day monitoring schedule.

Filter–weight was captured on 5 digits calibrated electronic balance (Sartorious, sensitivity of 0.01 mg) before and after sampling. Difference in weight of the filters between pre– and post– sampling yielded particulate mass. The prevalent ambient air temperature and humidity are described in the footnote of the tabulated data. Sampling for nine days was scheduled in the selected months. Data are represented as mean value ± SD µg/m^3 of 3 x 8 h values in triplicate.

2.3. Transmission Electron Microscope (TEM) study

Morphological features were studied using TEM. Only two fractions of submicron and nanosize (i.e. $PM_{0.56}$ and $PM_{0.056}$) were studied. Samples were suspended in sterile Milli–Q water and particles were spread on TEM grid. After drying, TEM image was captured. Shapes and sizes of $PM_{0.56}$ and $PM_{0.056}$ or their agglomerates were examined.

2.4. Metal analysis

The sampling in the spring was preferred due to comparatively greater traffic density. The samples (collected in Al foil) were washed and eventually suspended in aqua regia (HNO_3+HCL; 6:1 v/v). Metal concentrations were determined using the validated methods and Perkin Elmer atomic absorption spectrophotometer (AAS with graphite furnace). QA/QC was done by calibrating the instrument with multi–element Standard Reference Material (SRM) (Merck Chemicals). Quantification was done using calibration curves made from SRM of each metal. Empty Al foil without particles washed with an acid solution served as blank.

2.5. Fourier Transform Infrared spectroscopy (FTIR) study

The samples of autumn and winter season were studied (October 2011 and December 2011). The functional group compositions and bond information of adsorbed organic matter were analyzed using FTIR spectrometer (Nicolet Instruments Corporation, USA Model: MAGNA 550; wavelength 400–4000 1/cm). Particulate matter collection on Al foil was scratched to prepare Potassium bromide (KBr) pellet, and spectra were captured.

3. Results

3.1. Morphology

The study revealed shape, size, and agglomerated structures of superfine and ultrafine $PM_{0.56}$ and $PM_{0.056}$ fractions (Figure 2a and 2b). $PM_{0.56}$ was found to be formed of compact and spherical nanoparticles of varying sizes, i.e. $PM_{0.05}$ to $PM_{0.08}$ (Figure 2a). $PM_{0.056}$ and other nanosize particles existed as single and in fractal shape. However, in clustered and un–compacted form, $PM_{0.056}$ were spotted as shown in Figure 2b. $PM_{0.56}$ was found to be the cluster of 50–100 nm size particles. Similarly, $PM_{0.056}$ was seen to be the clusters of 10–100 nm size particles (Figure 2b).

3.2. Metal contents

Results of metal analyses in airborne ultrafine particulate matter are summarized in Table 1 and Figure 3. The toxic metals were found to be present in each size fraction. The distribution pattern of each metal is shown in Table 1. All the fractions contained Cd, Cr, Ni, Cu, Fe, and Pb (Table 1), comparatively, content of Fe was the greatest (Table 1). In general, metal contents were lower than their permitted exposure levels. Metals exhibited selectivity in distribution pattern with respect to particle size (Figure 3a to 3f). Fe accumulation was more in $PM_{1.8}$, $PM_{1.0}$, $PM_{0.18}$, $PM_{0.056}$ fractions and less in $PM_{0.56}$, $PM_{0.32}$, $PM_{0.1}$ fractions (Figure 3a). The contents of Ni in $PM_{1.8}$ to $PM_{0.1}$ exceeded the permitted levels marginally (Table 1). The contents of transitional metal Cu and Fe and toxic metal Pb were greater in $PM_{1.8}$ to $PM_{0.18}$ (Figure 4a and 4b).

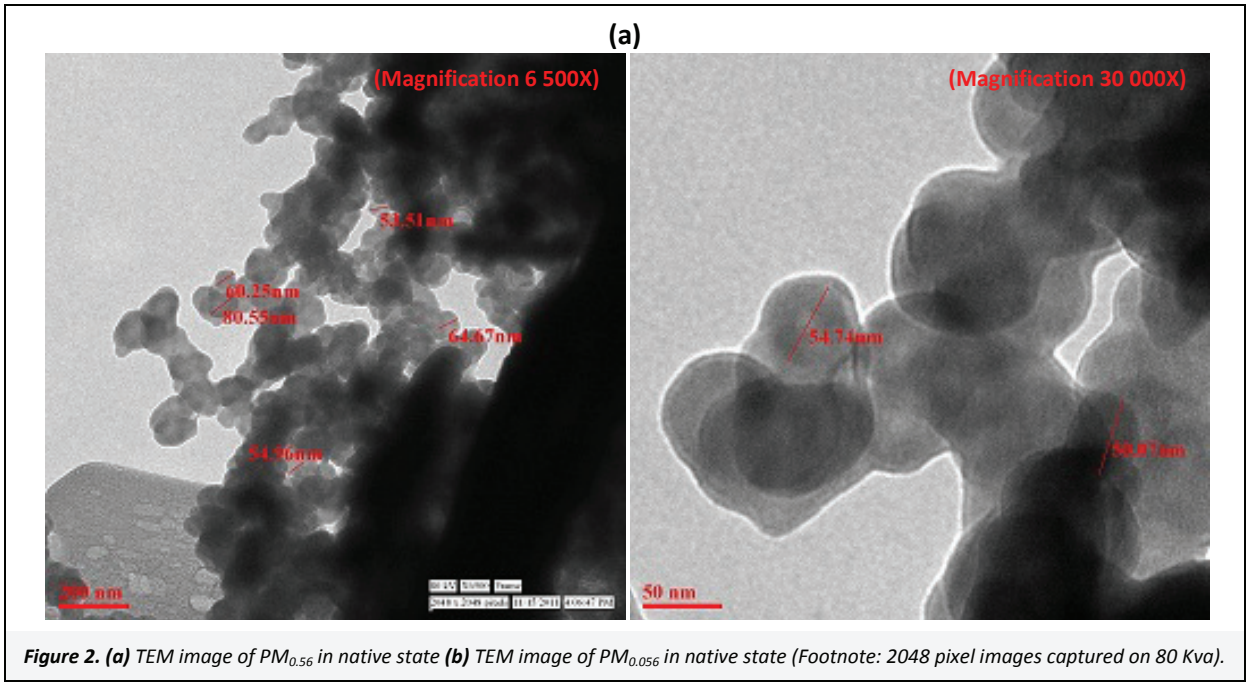

Figure 2. (a) *TEM image of $PM_{0.56}$ in native state* ***(b)*** *TEM image of $PM_{0.056}$ in native state (Footnote: 2048 pixel images captured on 80 Kva).*

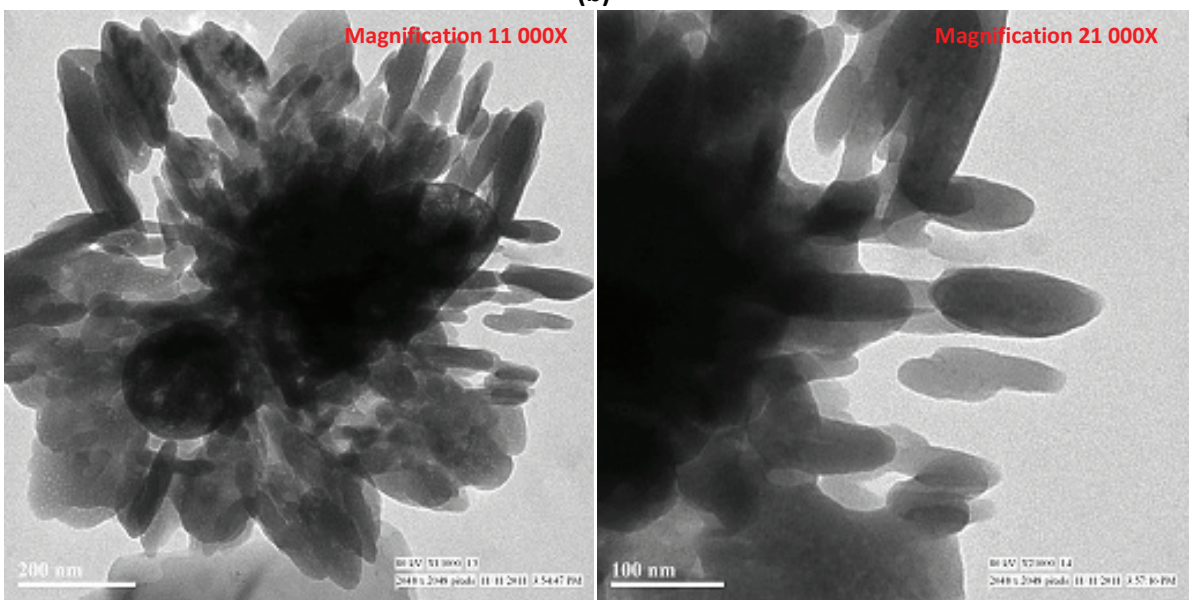

Figure 2. *(Continued).*

Table 1. *Ultrafine particle size based distribution of metal contents (Spring 2012)*

PM/Metal Contents	PM Size							Permissible Limit in Ambient Air	Reference	LOD (ng/mL)
	$PM_{1.8}$	$PM_{1.0}$	$PM_{0.56}$	$PM_{0.32}$	$PM_{0.18}$	$PM_{0.1}$	$PM_{0.056}$			
PM ($\mu g/m^3$)	25.59±14	16.43±2.44	17.74±2.73	17.54±5.71	11.72±3.7	6.16±1.0	8.31±5.2	60 $\mu g/m^3$	NA	NA
Cd (ng/m^3)	0.11±0.03	0.42±0.05	0.20±0.01	0.07±0.03	0.05±0.01	0.03±0.01	0.03±0.01	0.2 ng/m^3	U.S. EPA, 1999a	1.02
Cr (ng/m^3)	0.66±0.09	0.86±0.33	1.35±0.32	0.88±0.06	0.61±0.15	0.58±0.15	0.43±0.05	12 ng/m^3	U.S. EPA, 1999b	2.00
Ni (ng/m^3)	0.55±0.07	0.32±0.06	0.39±0.15	0.27±0.10	0.27±0.07	0.31±0.16	0.18±0.06	0.24 ng/m^3	U.S. EPA, 1999c	0.35
Cu (ng/m^3)	1.18±0.33	0.44±0.21	2.40±0.43	1.32±0.13	0.60±0.34	0.96±0.14	0.10±0.06	100 $\mu g/m^3$	NIOSH, 1997	0.29
Fe (ng/m^3)	259±8.90	185±3.70	80±12.71	31.48±17.08	160.8±16.34	43.51±9.8	112.73±20.9	10 mg/m^3	NIOSH, 1997	1.72
Pb (ng/m^3)	6.43±1.4	13.35±2.23	17.65±1.27	18.25±1.39	10.48±3.79	6.42±3.5	7.63±0.82	150 ng/m^3	U.S. EPA, 2008	10.00

Each metal accumulated to its maximum in a certain particle size. Ni and Fe accumulated in $PM_{1.8}$, Cd in $PM_{1.0}$, Cr and Cu in $PM_{0.56}$, Pb in $PM_{0.32}$ (Table 1). Accumulation of Cr, Cd, Ni, Pb, and transitional elements Cu and Fe were relatively more in submicron and less in nanosize particle (Figures 4a and 4b). $PM_{0.56}$ and $PM_{0.1}$ accumulated specifically most of Cr, Ni, Cu, Fe were present mostly in $PM_{1.8}$, PM_1, and $PM_{0.18}$ (Figure 4c and 4d). Generally, concentrations of metals were relatively higher than LOD (Limit of Detection) in each size fraction.

3.3. Organic chemical moieties

FTIR–based analyses of organic functional group distribution in each fraction are illustrated in Figures S1 and S2 (see the Supporting Material, SM) and listed in Table 2. Their absorption maxima showed a predefined position with variable intensity/peak–area depicting strong, moderate, or weak signal. Signal intensity of samples changed with the seasons.

A strong to weak presence of aliphatic hydrocarbons and alcohols was seen in all the size fractions sampled in winter or autumn (Table 2). Peaks at wave numbers 2 920–2 853 1/cm and around 1 460 1/cm characterized aliphatic hydrocarbons and C–H bonds respectively in autumn (Figure S1a–S1g) and winter (Figure S2a–S2g). Signal vibrations were noticed around 1 435–1 383 1/cm that displayed the bending and rocking of aliphatic chain. Aliphatic alcohols were characterized by wave numbers 3 200–3 600 1/cm and were found to be present in every fraction. A strong signal of aliphatic hydrocarbon was observed in $PM_{1.8}$, $PM_{1.0}$, and $PM_{0.56}$ in autumn, and that of aliphatic alcohol in $PM_{1.8}$ in both winter and autumn and in $PM_{1.0}$ in autumn only.

Peaks at 1 260 and 1 261 1/cm characterized the presence of organonitrate. A moderate to small quantity was detectable in $PM_{0.56}$ to $PM_{0.056}$ in autumn (Figure S1a–S1g). It was below detection limits in $PM_{1.8}$ and $PM_{1.0}$ (Table 2). Organonitrate signal was absent in particles sampled in winter (Figure S2–S2g).

Peaks in the range of 1 750–1 650 1/cm illustrated the presence of a carbonyl functional group. A strong to moderate levels of carbonyl compounds was seen in submicron size particles sampled in autumn (Figure S1a–S1g); it was below detection limits in micron size particles. In wintertime, the carbonyl functional group recorded a moderate presence in every size fraction (Figure S2a–S2g).

Peak at 1 595 1/cm signaled a strong to moderate presence of aromatic C=C stretch in all the size fractions in winter season (Figure S2a–S2g). The C=C structure was undetectable in autumn samples (Figure S1a–S1g).

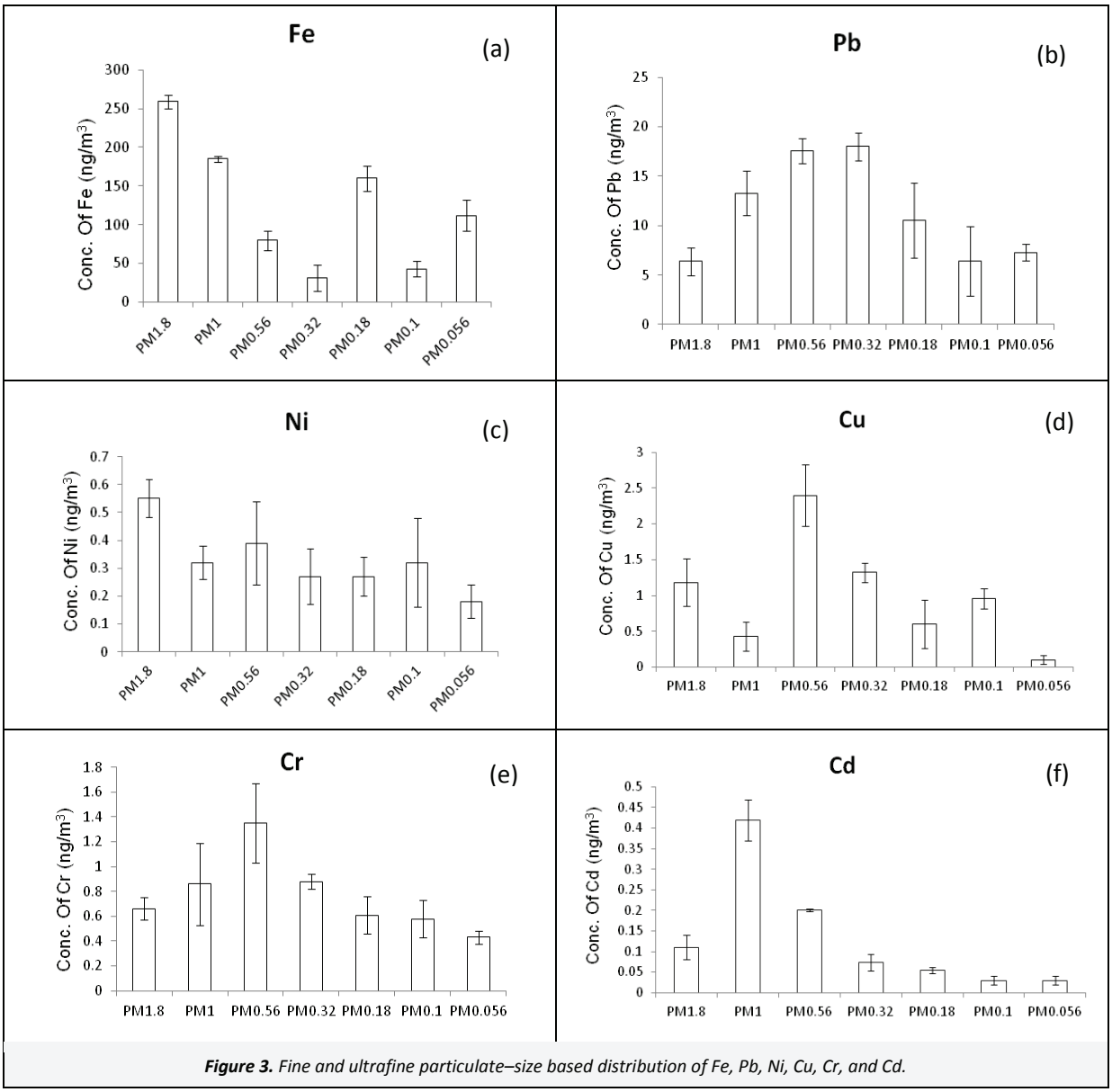

Figure 3. *Fine and ultrafine particulate–size based distribution of Fe, Pb, Ni, Cu, Cr, and Cd.*

Table 2. *Ultrafine particle size based organic chemical moieties and their seasonal variations*

PM Size	Aliphatic Hydrocarbon 2 920–2 853 and 1 435–1 383 1/cm		Aliphatic Alcohol 3 200–3 600 1/cm		Organonitrate 1 260–1 280 1/cm		Carbonyl/Ketone 1 700–1 750 1/cm		Aromatic Ring C=C stretch 1 595 1/cm	
	W [a]	A [b]	W	A	W	A	W	A	W	A
$PM_{1.8}$	++[d]	+++[e]	+++	+++	absent	absent	++	absent	+++	absent
PM_{1}	++	+++	++	+++	absent	absent	++	absent	+++	absent
$PM_{0.56}$	++	+++	+	++	absent	++	++	+++	+++	absent
$PM_{0.32}$	++	++	+	++	absent	+	++	+++	+++	absent
$PM_{0.18}$	++	+	++	+	absent	+	++	++	+++	absent
$PM_{0.1}$	+[c]	+	++	+	absent	++	++	++	++	absent
$PM_{0.056}$	+	+	++	+	absent	++	+	++	++	absent

[a] *Winter,* [b] *Autumn,* [c] *Weak,* [d] *Moderate,* [e] *Strong*

3.4. Mass concentrations

The values of micron, sub–micron, and nanoparticles in urban ambient aerosol are summarized in Table 3 and illustrated in Figure 5. The 8 h sampling between 8 AM to 4 PM yielded indeterminate PM_1 amounts. Only the sampling for 3 consecutive days yielded gravimetrically measureable quantity. Mass values were predominantly high in winter and low in the summer (Figure 5).

The mass concentrations of the studied fractions ranged between 2.74±0.86 to 74.52±22.14 μg/m^3. The concentrations varied with seasons. $PM_{0.56}$ and $PM_{0.32}$ recorded maximum mass concentrations in winter and $PM_{0.056}$ recorded lowest in summer (Table 3).

In winter, mass concentrations of $PM_{0.56}$, $PM_{0.32}$, $PM_{0.10}$, and $PM_{0.056}$ increased ~8–10 fold of their summer value. The largest increase was noticed in $PM_{0.56}$, and $PM_{0.32}$. Mass concentrations of the rest of the fractions were found to change by 2–4 folds from winter to summer. A trend of gradual decrease in mass concentrations was noticed in the entire set of fraction size range (i.e. $PM_{1.8}$ to $PM_{0.056}$) in every season (Figure 5) except $PM_{0.56}$ and $PM_{0.32}$. Mass of the individual fraction was greater also in spring however was lesser than the respective value in winter. In contrast, in autumn and summer, mass concentrations were consistent and differed insignificantly. The weather conditions in different seasons like ambient temperature, humidity, and wind speed and direction (Table 3) changed radically (4–6 fold) during sampling. The considerable variation in temperature from 9.6 to 41.40 °C, in humidity from 14 to 91%, and in wind velocity from 4 to 18 km/h was found to be associated with the change in mass concentrations.

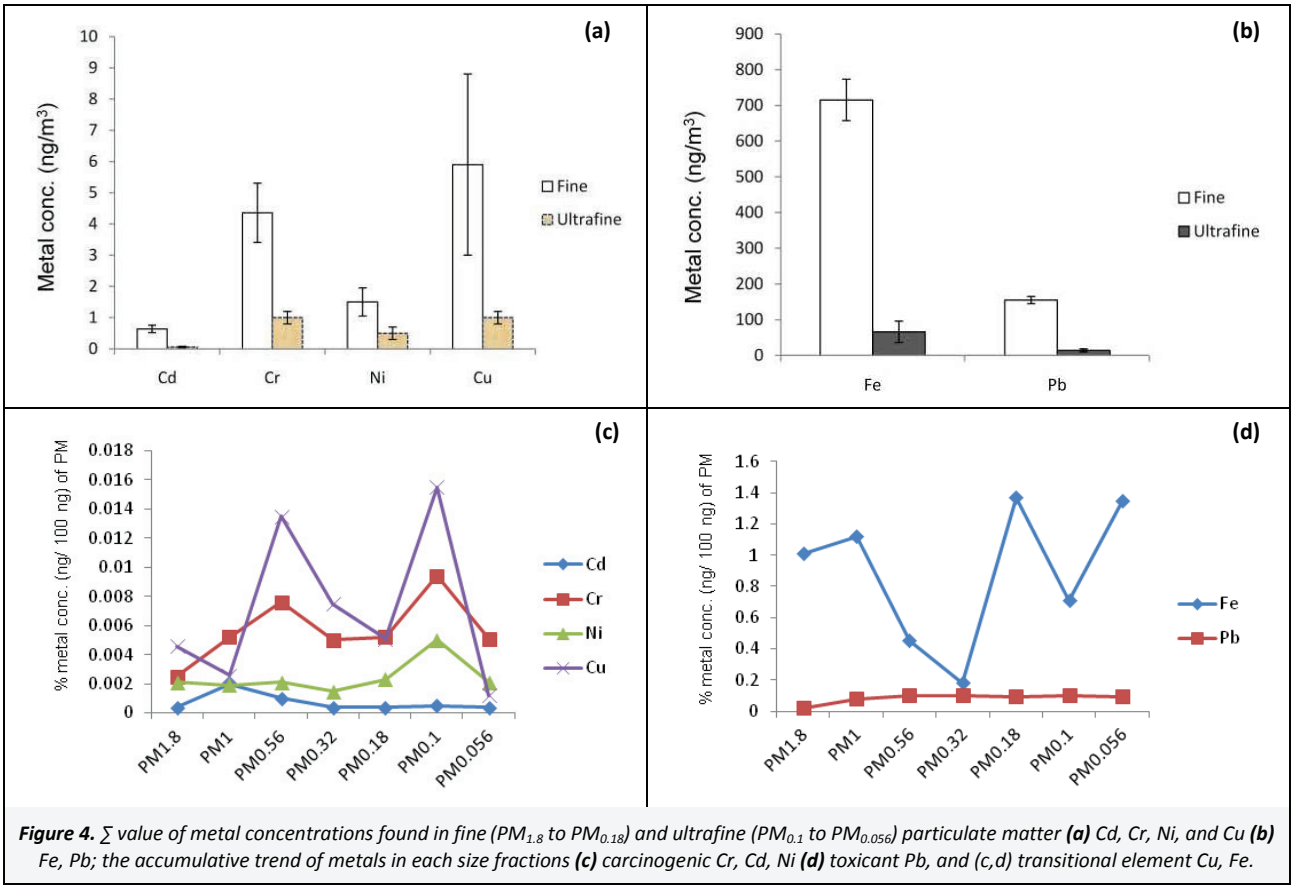

Figure 4. *∑ value of metal concentrations found in fine ($PM_{1.8}$ to $PM_{0.18}$) and ultrafine ($PM_{0.1}$ to $PM_{0.056}$) particulate matter* ***(a)*** *Cd, Cr, Ni, and Cu* ***(b)*** *Fe, Pb; the accumulative trend of metals in each size fractions* ***(c)*** *carcinogenic Cr, Cd, Ni* ***(d)*** *toxicant Pb, and (c,d) transitional element Cu, Fe.*

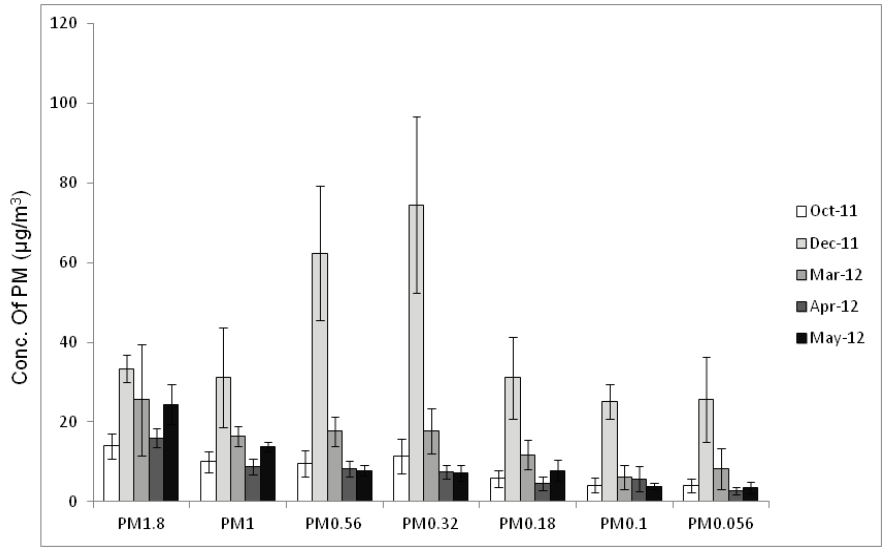

Figure 5. *Seasonal variation in mass concentrations of fine and ultrafine particulate matter in urban ambient air.*

Table 3. *Ultrafine particle size based mass concentrations and their seasonal variations*

PM Size	Month and Season of Monitoring				
	Oct–2011 [a] (Autumn) (μg/m^3)	Dec–2011 [b] (Winter) (μg/m^3)	Mar–2012 [c] (Spring) (μg/m^3)	Apr–2012 [d] (Summer) (μg/m^3)	May–2012 [e] (Summer) (μg/m^3)
$PM_{1.8}$	14±3.2	33.33±10.14	25.59±14	16±2.46	24.42±5
$PM_{1.0}$	10±2.7	31.15±12.54	16.43±2.44	8.82±1.91	13.77±1.14
$PM_{0.56}$	9.6±3.4	62.42±16.84	17.74±3.73	8.37±2.0	7.87±1.2
$PM_{0.32}$	11.4±4.3	74.52±22.14	17.74±5.71	7.56±1.7	7.16±1.9
$PM_{0.18}$	5.8±2.1	31.11±10.36	11.72±3.7	4.49±1.7	7.86±2.6
$PM_{0.10}$	4.15±1.9	25.12±4.33	6.16 ±1	5.75 ±3.1	3.8±0.1
$PM_{0.056}$	4.1±1.7	25.51±10.71	8.31±5.2	2.74±0.86	3.5±1.4

Values are mean ± SD of data from 9 days of 8 h monitoring; meteorological conditions during sampling:
Temperature (°C) 27±2.8[a], 9.6±1.8[b], 25±3.5[c], 34±4[d], 41.40±3.6[e]
Relative humidity (%)–42±15[a], 91±11.54[b], 46±20[c], 20±3[d], 14±6.6[e]
Wind speed (km/h)–13±2[a], 4.7±1[b], 14±6[c], 15±3[d], 18±4[e]

4. Discussion

This study has demonstrated ultrafine and superfine PM_1 mass concentrations, the adsorbed pro–oxidant chemicals, and their size distributed physicochemical properties in urban ambient air and their changes with seasons. The observed association of the low mass concentration with change of climate is a first report in literature. Major contributory factor seemed to be the season driven variation in traffic density of public transport and thus volume of the emitted exhausts, which was outwardly more in winter, spring, or autumn and relatively less in summer season. The information on shape and size, content of particulate matter and toxic metals, active moieties of organic chemicals, and their seasonal variability has indicated their association with automobile exhaust emissions.

The weather conditions can be hypothesized to alter the volatility of chemicals, agglomeration of aerosos, as well as their mass, and distort the results. Nonetheless, this limitation seems to be of minor importance because of the quantitative study of non–volatile metals and qualitative analyses of aerosolized volatile organic compounds. Xiong and Friedlander (2001) have found that in summer, freshly generated submicron particles in automobile exhaust exist in Aitken mode; and in winter these acquire accumulation mode after growing in size due to high humidity, and compaction.

Spherical shape of the agglomerated $PM_{0.56}$ fraction in urban ambient air is the result of accumulative tendency of fractal and irregularly shaped ultrafine PM. The fractal shape of $PM_{0.056}$ corresponds well with earlier observations reported in the literature (Loxham et al., 2013). Ultrafine particles i.e. $PM_{0.1}$ (primarily the products of incomplete combustion in exhaust emission) tend to be compacted to round–shape after ageing and condensation. These observations clearly relate the presence of studied PM fractions in urban aerosol with automobile exhaust pollution. The results suggest the probability of diesel and gasoline exhaust emissions being the primary source of ultrafine PM pollution in the sampled area.

The presence of carcinogenic metals Cd, Cr, Ni (IARC, 1990; IARC, 1997; Wang et al., 2006) and transition elements Cu and Fe in studied particulate fractions illustrates their hazardous potential. Contents of Cr, Ni, Cu, and Fe on submicron fractions are below the recommended and permissible exposure levels. Their levels, however, can be a health risk in view of pro–oxidant property and chronic exposures. A prolonged, inevitable, and continual exposure may induce oxidative stress and inflammation (Srivastava et al., 2011). These toxicants can enter lung alveoli through inhalation of the smudged $PM_{0.56}$ and $PM_{0.32}$ (the agglomerated fraction) and access target cells. These low–mass particles are reported to disable natural scavenging mechanisms locally at the particulate deposited site (Moller et al., 2002). This effect can extend the presence of particulate matter and the adsorbed toxicants in tissues for relatively longer duration to elicit adverse health effects (Kumar et al., 2013). Metals and hydrocarbon (both aliphatic and aromatic) in the ambient air $PM_{1.8}$–$PM_{0.056}$ is suggested to be of anthropogenic origin (Park et al., 2008; Lee et al., 1994; Chan et al., 2000; Singh et al., 2002; Manoli et al., 2002; Lu et al., 2011).

In the FTIR based study, the absorption peaks of aliphatic hydrocarbon indicate presence of isoprene (C_5H_8). Isoprene–derived epoxides are reported in ambient aerosol, and are described to form the hydroxylated, organosulfate, and organonitrate compounds (Darer et al., 2011) as also shown in our study.

Organonitrates are formed during reaction of volatile organic compounds. Their presence on submicron fractions ($PM_{1.0}$ to $PM_{0.056}$) is described for the first time. Further, it displays a role of low mass concentration and the adsorbed chemicals in secondary organic aerosol (SOA) formation. The organonitrate formation depends upon ambient air temperature and humidity. It is reflected in our studies also by the presence of organonitrate and aliphatic hydrocarbon in autumn and their absence in winter. The observed low level in winter is in accordance with the less formation of SOA reported under humid conditions (Zhang et al., 2011).

The detection of carbonyl groups on submicron and nanoparticles suggests the presence of ester, epoxides, and aldehyde/ketone compounds such as fatty acids in SOA (Guo and Bustin, 1998). Increases in contents of organic functional moieties in summer could to be the result of increased photochemical oxidation reactions on submicron particles (Miracolo et al., 2011). Increase in SOA formation in summer is also linked to the less condensation of semivolatile gas and hydrocarbons causing their continued presence in the gas phase as against particle phase in winter wherein the rapid reduction of gases lowers their availability and decreases the SOA formations (Schauer and Cass, 2000).

Our work shows a strong to moderate presence of both aromatic and aliphatic hydrocarbons in all the aerosol fractions and especially in winter. In autumn, signals of C=C stretch signifying the presence of aromatic rings could not be detected; therefore, only the aliphatic hydrocarbons seemed to be present on submicron particles. The absence of aromatic hydrocarbons in autumn may be due to their preferable association with particles of larger aerodynamic size (Naser et al., 2008). A steady change in temperature, humidity, wind velocity and direction during change of seasons can influence sampling of the low mass concentration and thus the exposure risks.

In essence, our study unveils significant information regarding (a) the baseline data on mass concentrations of micron, sub–micron, and nanosize fractions of urban aerosol, (b) profile of the adsorbed contents of transitional and carcinogenic metals as well as the functional moieties of organic chemicals, and (c) change in their concentrations with seasons. Presence of low levels of toxic metals in the studied PM fractions and their particle size based distribution pattern could confer the constituent particulates a pro–oxidant property and present a risk of toxicity or health hazard following the repeated and prolonged exposures in human subjects. Mass concentrations and pro–oxidant chemical profile of PM_1 have been rarely checked for ambient air quality survey in India or globally. These nonetheless need to be examined to develop a database on submicron and nanosize particulate matter and their seasonal variation pattern for urban ambient air quality monitoring and, if needed, for regulation of national ambient air quality standards (Lu et al., 2011; Loxham et al., 2013). The observations in this study are valuable for investigations on association of various health risks like cardiopulmonary/integu-mentary/sinus–mucosa disorders/atopic allergies with urban aerosol and the season dependent change in their clinical manifestations (Pleis and Lucas, 2009; Anderson et al., 2012; Kumar et al., 2013).

5. Conclusion

The mass concentrations of superfine and ultrafine (low–mass) matter and the adsorbed toxic metals are present in measurable quantity in urban ambient air environment. The study shows a strong presence of aliphatic hydrocarbons, organonitrates, carbonyl groups suggestive of isoprene and fatty acids in urban aerosol. The sampled low mass concentrations and the adsorbed chemicals are predominantly of anthropogenic origin, and possibly of transport –vehicle rubber–tyres, and the road–side kiosks origin. Speculatively, observed changes in the structures of PM_1 fractions and the levels of adsorbed chemicals with seasons can alter the physicochemical properties of the particulate pollutants and be detrimental to health of urban aerosol exposed subjects.

Acknowledgments

The authors are grateful to Director CSIR– Indian Institute of Toxicology Research, Lucknow for encouraging this study. Research Fellowship to one of the authors (MKV) by Indian Council of Medical Research New Delhi India is also gratefully acknowledged.

Supporting Material Available

FTIR spectroscopy of $PM_{1.8}$ to $PM_{0.056}$ in outdoor sample of autumn (October 2011) (Figure S1), FTIR spectroscopy of $PM_{1.8}$ to $PM_{0.056}$ fractions in outdoor sample of winter (December 2011) (Figure S2). This information is available free of charge via the Internet at http://www.atmospolres.com.

References

Anderson, J.O., Thundiyil, J.G., Stolbach, A., 2012. Clearing the air: A review of the effects of particulate matter air pollution on human health, *Journal of Medical Toxicology* 8, 166–175.

Chan, Y.C., Vowles, P.D., McTainsh, G.H., Simpson, R.W., Cohen, D.D., Bailey, G.M., McOrist, G.D., 2000. Characterisation and source identification of PM_{10} aerosol samples collected with a high volume cascade impactor in Brisbane (Australia). *Science of the Total Environment* 262, 5–19.

Darer, A.I., Cole–Filipiak, N.C., O'Connor, A.E., Elrod, M.J., 2011. Formation and stability of atmospherically relevant isoprene–derived organosulfates and organonitrates. *Environmental Science & Technology* 45, 1895–1902.

GOI (Government of India, Transport Research Wing, Ministry of Road Transport and Highways), 2013. Road Transport Yearbook 2011-2012, p. 4. http://morth.nic.in/showfile.asp?lid=1131; accessed in July, 2014.

Deshmukh, D.K., Deb, M.K., Mkoma, S.L., 2013. Size distribution and seasonal variation of size–segregated particulate matter in the ambient air of Raipur city, India. *Air Quality Atmosphere and Health* 6, 259–276.

Dockery, D.W., Pope, C.A., Xu, X.P., Spengler, J.D., Ware, J.H., Fay, M.E., Ferris, B.G., Speizer, F.E., 1993. An association between air–pollution and mortality in 6 United States cities. *New England Journal of Medicine* 329, 1753–1759.

Guo, Y.T., Bustin, R.M., 1998. Micro–FTIR spectroscopy of liptinite macerals in coal. *International Journal of Coal Geology* 36, 259–275.

IARC (International Agency for Research on Cancer), 1997. IARC monograph on the Evaluation of Carcinogenic Risk to Humans, Beryllium, Cadmium, Mercury, and Exposures in the Glass Manufacturing Industry Volume 58, WHO, Lyon, France.

IARC (International Agency for Research on Cancer), 1990. IARC Monograph on the Evaluation of Carcinogenic Risk to Humans, Chromium, Nickel and Welding, Volume 49, WHO, Lyon, France.

Kreyling, W.G., Semmler–Behnke, M., Moller, W., 2006. Ultrafine particle–lung interactions: Does size matter? *Journal of Aerosol Medicine–Deposition Clearance and Effects in the Lung* 19, 74–83.

Kumar, S., Verma, M.K., Srivastava, A.K., 2013. Ultrafine particles in urban ambient air and their health perspectives. *Reviews of Environmental Health* 28,117–28.

Lee, D.S., Garland, J.A., Fox, A.A., 1994. Atmospheric concentrations of trace–elements in urban areas of the United Kingdom. *Atmospheric Environment* 28, 2691–2713.

Loxham, M., Cooper, M.J., Gerlofs–Nijland, M.E., Cassee, F.R., Davies, D.E., Palmer, M.R., Teagle, D.A.H., 2013. Physicochemical characterization of airborne particulate matter at a mainline underground railway station. *Environmental Science & Technology* 47, 3614–3622.

Lu, S.L., Feng, M., Yao, Z.K., Jing, A., Yufang, Z., Wu, M.H., Sheng, G.Y., Fu, J.M., Yonemochi, S., Zhang, J.P., Wang, Q.Y., Donaldson, K., 2011. Physicochemical characterization and cytotoxicity of ambient coarse, fine, and ultrafine particulate matters in Shanghai atmosphere. *Atmospheric Environment* 45, 736–744.

Manoli, E., Voutsa, D., Samara, C., 2002. Chemical characterization and source identification/apportionment of fine and coarse air particles in Thessaloniki, Greece. *Atmospheric Environment* 36, 949–961.

Mauderly, J.L., Chow, J.C., 2008. Health effects of organic aerosols. *Inhalation Toxicology* 20, 257–288.

Meister, K., Johansson, C., Forsberg, B., 2012. Estimated short–term effects of coarse particles on daily mortality in Stockholm, Sweden. *Environmental Health Perspectives* 120, 431–436.

Miracolo, M.A., Hennigan, C.J., Ranjan, M., Nguyen, N.T., Gordon, T.D., Lipsky, E.M., Presto, A.A., Donahue, N.M., Robinson, A.L., 2011. Secondary aerosol formation from photochemical aging of aircraft exhaust in a smog chamber. *Atmospheric Chemistry and Physics* 11, 4135–4147.

Moller, W., Hofer, T., Ziesenis, A., Karg, E., Heyder, J., 2002. Ultrafine particles cause cytoskeletal dysfunctions in macrophages. *Toxicology and Applied Pharmacology* 182, 197–207.

Naser, T. M., Yoshimura, Y., Sekiguchi, K., Wang, Q., Sakamoto, K., 2008. Chemical composition of $PM_{2.5}$ and PM_{10} and associated polycyclic aromatic hydrocarbons at a roadside and an urban background area in Saitama, *Japan Asian Journal of Atmospheric Environment*, 2, 90–101.

NIOSH (National Institute for Occupational Safety and Health), 1997. Pocket Guide to Chemical Hazards, U.S. Department of Health and Human Services, Public Health Service, Centres for Disease Control and Prevention. Cincinnati. http://www.cdc.gov/niosh/npg/npgd0344.html, accessed in April 2014.

Oberdorster, G., Utell, M.J., 2002. Ultrafine particles in the urban air: To the respiratory tract – and beyond? *Environmental Health Perspectives* 110, A440–A441.

Park, K., Heo, Y., Putra, H.E., 2008. Ultrafine metal concentration in atmospheric aerosols in urban Gwangju, Korea. *Aerosol and Air Quality Research* 8, 411–422.

Pleis, J.R., Lucas, J.W., 2009. Summary Health Statistics for U.S. Adults: National Health Interview Survey, 2007, Hyattsville, Maryland, 171 pages.

Roberts, R.A., Smith, R.A., Safe, S., Szabo, C., Tjalkens, R.B., Robertson, F.M., 2010. Toxicological and pathophysiological roles of reactive oxygen and nitrogen species. *Toxicology* 276, 85–94.

Schauer, J.J., Cass, G.R., 2000. Source apportionment of wintertime gas–phase and particle–phase air pollutants using organic compounds as tracers. *Environmental Science & Technology* 34, 1821–1832.

Singh, M., Jaques, P.A., Sioutas, C., 2002. Size distribution and diurnal characteristics of particle–bound metals in source and receptor sites of the Los Angeles basin. *Atmospheric Environment* 36, 1675–1689.

Srivastava, A.K., Kesavachandran, C.N., Kumar, S., 2011. Evaluating risks of acquired clinical vulnerability among subjects exposed to E–waste. *Reviews of Environmental Contamination and Toxicology,* 214, 1–14.

Stone, V., Johnston, H., Clift, M.J.D., 2007. Air pollution, ultrafine and nanoparticle toxicology: Cellular and molecular interactions. *IEEE Transactions on Nanobioscience* 6, 331–340.

Strak, M., Janssen, N.A.H., Godri, K.J., Gosens, I., Mudway, I.S., Cassee, F.R., Lebret, E., Kelly, F.J., Harrison, R.M., Brunekreef, B., Steenhof, M., Hoek, G., 2012. Respiratory health effects of airborne particulate matter: The role of particle size, composition, and oxidative potential–the RAPTES project. *Environmental Health Perspectives* 120, 1183–1189.

U.S. EPA (U.S. Environmental Protection Agency), 2008. National Ambient Air Quality Standard, The 1978 lead standard (1.5 μg/m^3 as a quarterly average). http://www.epa.gov/air/criteria.html, accessed in April 2014.

U.S. EPA (U.S. Environmental Protection Agency), 1999a. Integrated Risk Information System (IRIS) on Cadmium. National Center for Environmental Assessment, Office of Research and Development, Washington, DC.

U.S. EPA (U.S. Environmental Protection Agency), 1999b. Integrated Risk Information System (IRIS) on Chromium VI, National Center for Environmental Assessment Office of Research and Development, Washington, DC.

U.S. EPA (U.S. Environmental Protection Agency), 1999c. Integrated Risk Information System (IRIS) on Nickel Refinery Dust, National Center for Environmental Assessment, Office of Research and Development, Washington, DC.

Valavanidis, A., Vlachogianni, T., Fiotakis, K., Loridas, S., 2013. Pulmonary oxidative stress, inflammation and cancer: Respirable particulate matter, fibrous dusts and ozone as major causes of lung carcinogenesis through reactive oxygen species mechanisms. *International Journal of Environmental Research and Public Health* 10, 3886–3907.

Voutsa, D., Samara, C., 2002. Labile and bioaccessible fractions of heavy metals in the airborne particulate matter from urban and industrial areas. *Atmospheric Environment* 36, 3583–3590.

Wang, X.H., Bi, X.H., Sheng, G.Y., Fu, H.M., 2006. Hospital indoor $PM_{10}/PM_{2.5}$ and associated trace elements in Guangzhou, China. *Science of the Total Environment* 366, 124–135.

WHO (World Health Organization), 2006. Air Quality Guidelines: Global Update 2005: Particulate Matter, Ozone, Nitrogen Dioxide, and Sulfur Dioxide; World Health Organization: Copenhagen, Denmark.

Xiong, C., Friedlander, S.K., 2001. Morphological properties of atmospheric aerosol aggregates. *Proceedings of the National Academy of Sciences of the United States of America* 98, 11851–11856.

Zhang, H., Surratt, J.D., Lin, Y.H., Bapat, J., Kamens, R.M., 2011. Effect of relative humidity on soa formation from isoprene/no photooxidation: Enhancement of 2–methylglyceric acid and its corresponding oligoesters under dry conditions. *Atmospheric Chemistry and Physics* 11, 6411–6424.